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ABSTRACT

Studies of junction photoluminescence in CdTe/CdS solar cells reveal that back-contact application produces a dramatic qualitative change in the junction PL spectrum. Prior to contact application, the spectrum has two peaks at energies of 1.508 eV and 1.45 eV, corresponding to recombination in bulk CdTe, and in a CdTeS alloy with 9% sulfur content, respectively. After contact application, the spectrum consists of a single broad peak at 1.48 eV. Previous studies have shown that the nitric-phosphoric (NP) etch used in the contact procedure produces a layer of elemental Tellurium (Te) on the CdTe surface. Our measurements utilizing Auger electron spectroscopy (AES) show that this Te layer penetrates grain boundaries down to the CdTe/CdS interface. It appears that the change in the near-junction PL spectrum is caused by a "grain boundary field effect" due to perturbations of the grain boundary conductivity and Fermi level.

INTRODUCTION

One of the critical issues in the production of thin-film CdTe/CdS photovoltaic devices is the ability to form low resistance ohmic contacts to p-type CdTe. Various surface treatments are applied prior to deposition of a metallic contact. One of the most effective is the use of a nitric-phosphoric (NP) acid etch.^[1] It has been shown that the NP etch preferentially etches grain boundaries, and that this etch produces a layer of elemental Te on the surface of the CdTe grains.^[2] Issues of how the back contact affects the stability of CdTe/CdS PV modules have recently arisen. In light of the key role played by the back contact, it is important to further our understanding of how these contacts work and how back-contact treatments affect the CdTe material itself. Measurements of photoluminescence spectra on numerous close-spaced sublimation (CSS) CdTe/CdS devices grown at NREL

have found that the application of a back contact produces a significant qualitative change in the junction PL spectrum. This study examines the nature and causes of these changes.

EXPERIMENTAL

Samples

We have studied the effect of numerous back contact treatments on the observed ps-PL spectrum for the CdTe adjacent to the CdTe/CdS interface. Samples in this study consist of standard NREL CSS-CdTe / CBD-CdS / SnO₂ / 7059 glass. The CdTe thickness is approximately 10 μm with a grain size of about 3 μm . We have studied samples both with and without the post-growth CdCl₂ - heat treatment. Although PL intensity is higher in CdCl₂ treated samples, the spectral properties are the same with and without treatment. We have studied a matrix of back contact treatments including NP etch only, NP etch followed by annealing, NP etch followed by HgTe/graphite paste, HgTe/graphite paste alone, then with annealing, application of silver conducting paint, and finally, evaporated Te. We have also studied the effects of using ion beam milling to remove several microns of CdTe from the back surface of the sample after these treatments.

Photoluminescence

Typical room-temperature PL measurements on polycrystalline CdTe (px-CdTe) are dominated by recombination at defects because of the high density of defect states relative to the photoexcited carrier density. The PL spectra described in this study are unique in that a cavity-dumped dye laser is used as the excitation source. The laser provides pulses 5 picoseconds long at a repetition rate of 1 MHz. Due to the extremely low duty cycle of the laser we are able to inject much higher photoexcited carrier densities than is practical with a CW laser. Initial carrier densities immediately after the laser pulse are approximately $4 \times 10^{16} \text{ cm}^{-3}$. By comparison, typical densities for CW PL measurements are on the order of $2 \times 10^{13} \text{ cm}^{-3}$, while AM1.5 solar conditions produce approximately $2 \times 10^{11} \text{ cm}^{-3}$.^[3] Hereafter we will refer to these pulsed, high excitation PL measurements as ps-PL. Photoexcitation is through the transparent CdS window layer at a wavelength of 600nm. The 1/e penetration depth for this wavelength in CdTe is 0.2 μm . Numerical modeling indicates that over 90% of the photoexcited carriers recombine within the first 1 μm of CdTe adjacent to the CdTe/CdS interface, hence the term

junction photoluminescence. The measurement is conducted at 300K under open circuit conditions. Spectral resolution is 1 nm, which corresponds to approximately 2 meV in the wavelength range of interest.

PL Results

The typical junction ps-PL spectrum for NREL CSS-CdTe/CdS material prior to contact application is shown as the solid line in Fig. 1. There is a main peak at 1.455 eV and a shoulder at 1.49 eV. We have used Voigt lineshape functions to fit this PL spectrum with two peaks at 1.45 eV and 1.508 eV. The higher energy peak precisely matches the peak energy of ps-PL measured on the back side of the CdTe layer, and is identified as band-to-band recombination in px-CdTe. The lower energy peak has previously been identified as band-to-band recombination in a region of CdTeS alloy formed near the CdTe - CdS interface due to diffusion of sulfur into the CdTe layer.^[4] The peak energy of 1.45 eV corresponds to an alloy with 9% sulfur content.^[5] We have confirmed these peak assignments by studying the density-dependence of the ps-PL spectrum. Both peaks increase equally in intensity as the laser intensity is increased. No other peaks appear as the photoexcited carrier density is increased up to 10^{18}cm^{-3} . If the observed ps-PL peaks were due to recombination through impurities or defects we would expect to see a higher-energy band-to-band peak appear at such high densities. Since this does not occur we conclude that the two observed peaks are due to band-to-band recombination in regions of CdTe, and a 9% CdTeS alloy.

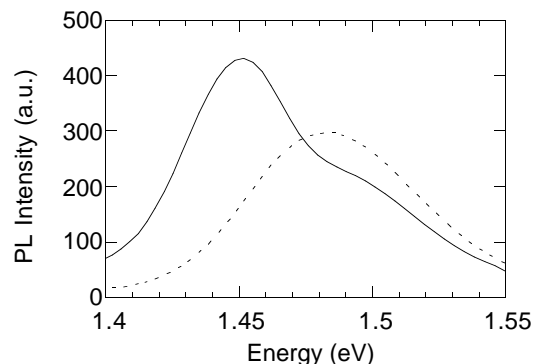


Fig. 1 Junction ps-PL spectra for an NREL CdTe/CdS device structure before (solid line) and after contact application (dashed line).

The dashed line in Fig. 1 shows the ps-PL spectrum for the same sample after contact application. It is important to note that the ps-PL measurement probes 1 μm of CdTe adjacent to the CdTe/CdS interface, while the contact is applied to the back of the sample, 10 μm away. The spectrum consists of what appears to be a single broad peak at 1.48 eV. We have attempted to fit this peak with a wide variety of fitting functions. The asymmetry of the peak is such that the best fit is achieved using two Voigt lineshapes with peak energies of 1.509 eV and 1.487 eV. The peak at 1.509 eV is consistent with PL from px-CdTe, while the lower energy peak matches the band gap of a CdTeS alloy with approximately 3% sulfur. The alloy PL peak intensity has decreased relative to the CdTe peak.

The standard NREL method for applying back contacts is to first etch the back surface with a nitric-phosphoric acid (NP) etch. Then a HgTe-doped graphite paste is applied and the sample is annealed. Finally silver paste is applied to form the metallic contact. By measuring ps-PL spectra at each step in this process we found that the change in the spectrum is produced by NP etch without annealing. Measurements of ps-PL on the back surface of an etched CdTe/CdS device showed a decrease in PL intensity, but no change from the single 1.508 eV ps-PL peak observed prior to NP etch. This is good evidence that the two-peak ps-PL spectrum on the junction side is associated with the presence of CdTeS alloy and not just a defect level produced by the NP etch at the grain boundary.

As a further test of our interpretation of the post-NP etch spectrum being composed of two peaks we have monitored the ps-PL as a function of incremental steps of NP etch time. The typical NP etch procedure for NREL CdTe/CdS cells requires a 40 second etch time. Fig. 2 presents ps-PL spectra for etch times of 0, 10, 20, and 30 seconds. Beyond 30 seconds of etch time there is very little change in the spectrum. It is clear from this data that the change in PL produced by the NP etch is not a binary, "on or off" effect. Rather, the shift from two peaks to one is gradual and is consistent with increasing thickness and depth of Te layers in the grain boundaries.

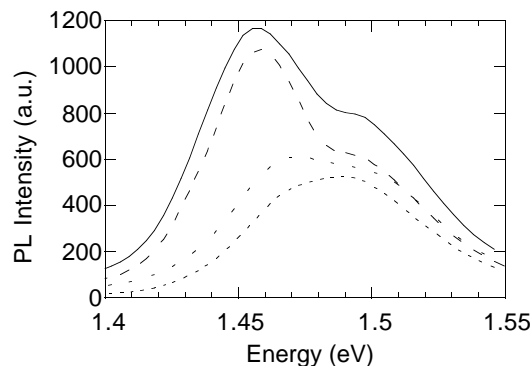


Fig. 2 Junction ps-PL spectra showing evolution of spectra with increments of NP etch time. Etch times of 0, 10, 20, and 30 seconds correspond to solid, large dash, medium dash, and smallest dashed lines. For clarity the intensities have been scaled to avoid overlap.

A study of NP etch effects on single-crystal CdTe has found that a 60 second NP etch removes Cadmium, leaves 30 nm of elemental Te on the CdTe surface, and produces a transition region of Te-rich CdTe of 50 nm thickness.^[6] According to the Landolt-Bornstein tables Te is a degenerate p-type semiconductor with a band gap of 0.33 eV.^[7] The study of NP-etched CdTe surfaces also used evaporation to apply Te to the surface of px-CdTe and found that the Fermi level of Te layers less than 26 Å thick was pinned by the midgap surface states of the CdTe grain and thus the layer was n-type. The Te layers greater than 76 Å thick were degenerate p-type. The primary distinctions between NP etch and evaporated Te are that NP etch preferentially etches grain boundaries and produces a 50 nm thick transition region of Te-rich CdTe,

while evaporation produces an abrupt interface between Te and CdTe.

To determine whether or not the Te layer produced by the NP etch is responsible for the change of the ps-PL spectrum we investigated several other back surface treatments. Application of silver conducting paint to the back surface had no effect on the junction ps-PL spectrum. Bromine-methanol (Br-Me) is an etch for CdTe which is known to leave a Te-rich surface. Upon etching an NREL CdTe/CdS device structure we found that Br-Me produces the same shift in the junction PL as that observed for NP etch. X-ray photoelectron spectroscopy (XPS) measurements confirm the Br-Me etched surface is elemental Te. We also used vacuum evaporation to deposit a 50 nm layer of Te on the back surface of a CdTe/CdS device structure and observed a change in the ps-PL spectrum identical to that observed for NP and Br-Me etches.

At this point it is reasonable to conclude that the Te layer is causing the change in the ps-PL. The key question is whether the change is a grain boundary effect or a back surface field effect. The fact that evaporated Te produces the spectral shift would indicate that it is a back surface field effect. We have utilized the device simulation program SimWindows to model the effects of a degenerate p-type layer on the back surface of a CdTe/CdS device. In this numerical simulation the back surface field produced by a contact does not perturb photoexcited carrier distributions at the junction. This makes it unlikely that the observed effect is due to a back surface field.

To further test this hypothesis we have used ion beam milling to remove the layer of Te from the back surface. Fig.3 shows ps-PL spectra for samples which have milling depths of 0, .18, .72, 1.26, and 2.6 μm . As can be seen in the figure, and has been verified by peak fitting, the 0.18 μm spectrum is unchanged from the NP etched spectrum, while each successive step in milling changes the spectrum more and more towards that observed for non-etched samples. The 2.6 μm sample has a spectrum which matches that for a non-etched sample. XPS measurements of the ion-milled surfaces show that the 0.18 μm sample is stoichiometric CdTe, while the longer milling times become increasingly Cd-rich at the back surface.

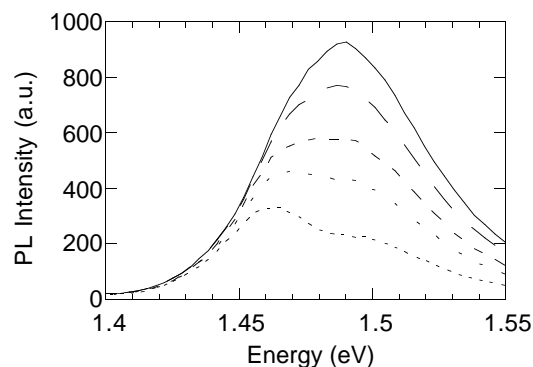


Fig. 3 Evolution of the junction ps-PL spectrum with ion beam milling depth. The five spectra in the figure are for

milling depths of 0, 180 nm, 720 nm, 1.26 μm , and 2.6 μm . Smaller dashed lines correspond to increased milling time. For clarity the intensities have been scaled to avoid overlap.

The fact that the PL spectrum of the 0.18 μm milled sample is unchanged confirms the results of our device modeling, namely that the effect on the junction PL spectrum is not a back surface field effect. The interpretation of the gradual return to a non-etched spectrum is more complicated. Such behavior with milling depth would be consistent with relatively thick layers of elemental Te in the grain boundaries near the back surface, with decreasing thickness moving towards the front of the device. Thick, degenerate p-type grain boundaries near the back surface, together with the highly conductive Te layer down the grain boundaries, could affect the Fermi level of grain boundaries near the junction region where the junction ps-PL originates. As the thick Te layers are removed from the back, the Fermi level of the grain boundaries again become pinned to the midgap surface states of the CdTe grain surface just as prior to NP etch. Thus, the thin Te grain boundary layers down near the junction become less p-type and eventually may be converted to n-type.

Auger Electron Spectroscopy (AES)

We have made extensive use of AES in both depth profiles and surface maps to characterize the composition of various px-CdTe films used in this study. Fig. 4 presents a high-contrast surface map of the relative intensity of the Te AES signal.

This image is from the back surface of an NP etched sample after sputtering 30 nm of material off of the back to remove the elemental Te layer. The dark areas are

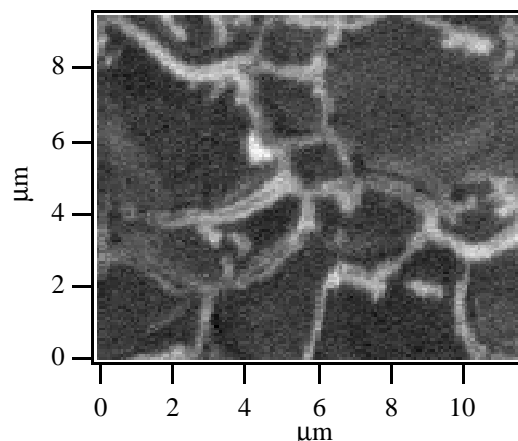


Fig. 4 Auger electron spectroscopy map of Te composition on back surface of NP-etched px-CdTe/CdS PV device structure. Dark areas are stoichiometric CdTe within grains, while light areas are grain boundaries with approx. 75:25 Te:Cd ratio. AES probe diameter is 40 nm.

stoichiometric CdTe, while the bright areas are high Te content. The dark areas correspond to the interior of the grains while the light areas are the grain boundaries.

Using a 40 nm diameter electron beam, AES indicates a ratio of 75:25 Te: Cd in the grain boundaries. It is likely that the beam diameter exceeds the grain boundary dimensions, and the Te: Cd ratio within the grain boundary could be higher than that measured by AES. This image is clear evidence that the NP etch produces Te-rich, or pure Te grain boundaries at the back surface.

Obtaining measurements of grain boundary composition near the CdTe/CdS interface has proven very difficult. Attempts to sputter down from the back surface fail due to rapid degradation of film morphology with sputter depth. We have managed to "lift-off" some CdTe films from the CdS layer, providing direct access to this interface. Although technical difficulties have prevented us from obtaining compositional maps like the one in Fig. 4, we

have measured an AES depth profile from the front surface of the CdTe layer. Such a profile is shown in Fig. 5 for a sample which has undergone 90 seconds of NP etch. It is important to note that the composition profile is a large-area scan over many grains and grain boundaries, and thus presents an average of grain and grain boundary composition. Te content is less than 50% near the interface due to sulfur diffusion into the CdTe, but away from the interface it is clear that the material is Te-rich.

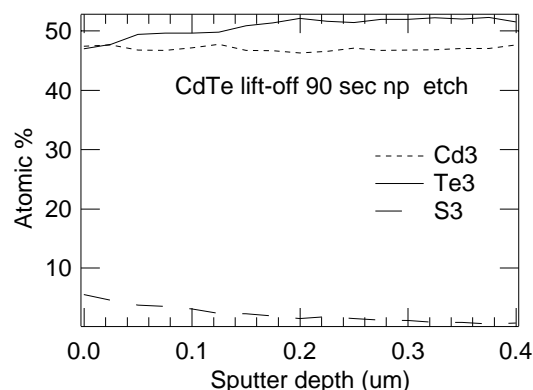


Fig. 5 AES compositional depth profile of CdTe "lift-off" film showing Cd, Te, and S atomic percentages. This profile begins at the CdTe/CdS interface and moves towards the back of the CdTe film.

This measurement required an extreme NP etch time of 90 seconds to produce a measurable Te excess due to the averaging over grains and grain boundaries. This is clear evidence that the NP etch can produce Te-rich grain boundaries all the way through the CdTe layer to the CdTe/CdS interface.

Conclusions

We have provided extensive evidence that the qualitative change in the junction ps-PL spectrum associated with the NP etch process is caused by the accumulation of elemental Te in the grain boundaries. How this perturbation of the PL spectrum comes about is not completely clear at this time. We can postulate a model of the recombination process which produces the two-peak PL spectrum and of how the presence of elemental Te in the grain boundaries could perturb the PL spectrum.

Generally accepted models hold that charged defects and impurities segregated at grain boundaries will produce a depletion layer at the grain boundary.^[8] The Fermi level in such a grain boundary will be near mid-gap. After the NP etch process there will be a layer of elemental Te, which if thick enough, will be degenerate p-type. This is a large perturbation of the position of the Fermi level and also a major increase in the conductivity of the grain boundary. These changes will in turn produce significant changes in the electric fields and carrier distributions in the near-grain boundary regions of the interior of the grain.

Numerous studies have shown that inter-diffusion across the CdTe - CdS interface produces a thin (200 - 300 nm) layer of CdTeS alloy on the CdTe side of the interface.^[9]

Recent energy dispersive x-ray analysis measurements (EDS) have shown that the sulfur content within a CdTe grain near the CdTe/CdS interface has a radial dependence, with the highest concentration at the grain boundary and a rapid decrease moving towards the center of the grain.^[10]

This structural information brings us to a model for the ps-PL spectra we have observed. Prior to the NP etch treatment, recombination occurs throughout the grain. After NP etch the population of one or both carrier types is depleted near the grain boundary and recombination shifts towards the center of the grain. The net effect is that the percentage of PL originating in pure CdTe will increase, while the average sulfur content of the CdTeS participating in recombination processes will decrease. Thus, the post-NP etch PL spectrum should have a decrease in the amplitude of the lower energy, CdTeS alloy peak, and this peak should shift towards higher energy. This is completely consistent with all of the observations reported in this study.

Implications

The conclusions of this research study imply a three dimensional nature to carrier collection in px-CdTe/CdS solar cells. Degenerate p-type grain boundaries penetrating either partially or fully through the absorber layer will function as majority carrier collection pathways.

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